Fundamental redox processes of coinage metals in cross coupling catalysis

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The mechanistic understanding of transition metal-catalyzed chemical transformations is of fundamental importance to design optimized methodologies for the synthesis of target products. We are interested in coinage metal catalysis, with special focus in unravelling the detailed molecular mechanisms and redox chemistry involved in C-C and C-heteroatom cross-coupling reactions. Here we present the unprecedented isolation of elusive aryl-copper(III)-halide species directly involved in C-heteroatom catalytic reactions using model aryl halide substrates. In situ spectroscopic studies of Cu-catalyzed C-X (X= F, Cl, Br, I), C-N, C-O, C-S, C-Se, C-P and C-C coupling reactions provides definitive evidence for the involvement of an aryl-copper(III)-halide intermediate in a redox Cu(I)/Cu(III) catalytic mechanism.[1] On the other hand, analogous two-electron redox catalytic cycles, which are most common in noble metal organometallic reactivity, have never been considered for Ag. Herein, we show that an unprecedented Ag(I)/Ag(III) catalytic cycle is operative in model C-O and C-C cross-coupling reactions.[2] We anticipate our study as the starting point for expanding Ag(I)/Ag(III) redox chemistry into new methodologies for organic synthesis, resembling well-known copper or palladium cross-coupling catalysis. Furthermore, findings described herein dismiss the generally accepted conception that silver redox chemistry can only arise from one electron processes. Finally, we present our latest results in exploring the unprecedented oxidant-free Au(I)-catalyzed cross coupling reactions.

[1] a) Casitas, A.et al. Chem. Sci. 2013, 4, 2301-2318; b) Casitas, A. et al. Chem. Sci. 2010, 1, 326-330; c) Huffman L. M. et al. Chem. Eur. J., 2011, 17, 10643-10650; d) Font, M. et al. Organometallics 2012, 31, 7976−7982; e) Casitas, A. et al. J. Am. Chem Soc. 2011, 133, 19386–19392.
[2] M. Font, et al. Nat. Commun. 2014, 5:4373 | DOI: 10.1038/ncomms5373.